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Hydrogen-halogen chemistry on semiconductor surfaces

by

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Hydrogen-halogen chemistry on semiconductor surfaces

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Abstract

The chemistry of coadsorbed H and X (X=Cl, Br) on semiconductor surfaces is important in epitaxial growth of silicon from chlorosilanes and of $\text{Si}_x\text{Ge}_{1-x}$ alloys, in hydrogenating/halogenating cycles in atomic layer epitaxy, and also provides an interesting model system, yet has received little attention to date. We have investigated the interaction of H, HCl, and HBr with Ge(100) by temperature-programmed desorption, and find that H_2 , HCl, and HBr *each* desorb with near-first-order kinetics near 570-580 K, and that GeCl_2 and GeBr_2 desorb with second-order kinetics near 680 K and 710 K, respectively. Trends in the chemistry and kinetics can be rationalized by viewing the dimer atoms on clean Ge(100)-(2×1) as being linked by a strained double bond and adsorption, decomposition, and desorption as being analogous to addition, rearrangement, and elimination reactions of molecular germanium compounds. The near-first-order desorption kinetics are attributed to pairing on surface dimers induced by the π bond on unoccupied dimers. We infer a pairing enthalpy for H+H (\approx the π bond strength of dimerized Ge(100) surface atoms) of 4-5 kcal/mol.

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I. INTRODUCTION

There is currently great interest in the growth by atomic layer epitaxy (ALE) of the group IV semiconductors diamond, silicon, and $\text{Ge}_x\text{Si}_{1-x}$ alloys. Two ALE processes for silicon have been demonstrated, involving alternating halogenated-precursor/hydrogen [1] or Si_2H_6 /photothermally-induced H_2 desorption [2] cycles. Both processes involve surface hydrogen in one self-terminating step, and the first utilizes surface chlorine to terminate the growth step [1]. In addition, chlorosilane chemical vapor deposition (CVD), which involves surface hydrogen and chlorine as intermediates, has been the dominant epitaxial silicon growth technology for twenty years. The surface chemistry of hydrogen and of coadsorbed hydrogen and halogens thus plays a central role in both the ALE and CVD of Si and of $\text{Ge}_x\text{Si}_{1-x}$.

In this paper we investigate the interaction of H, HCl and HBr with Ge(100) by temperature-programmed desorption (TPD) for the first time, focusing on the adsorption kinetics of HCl and HBr and the desorption kinetics of H_2 , HCl, HBr, GeCl_2 , and GeBr_2 .

II. EXPERIMENTAL

Experiments were performed in a custom-built vacuum chamber [3] (base pressure $\approx 1 \times 10^{-10}$ Torr), pumped via a liquid- N_2 -trapped diffusion pump and titanium sublimation pump, and equipped with LEED/ESDIAD optics, an Auger spectrometer (VSW hemispherical analyzer HA-100), infrared optics, a VG SXP-400 quadrupole mass spectrometer (QMS) with a water-cooled shroud mounted on a translation system, a calibrated gas doser [4], an ion gun, and a tungsten filament used for dosing of atomic hydrogen. The sample holder was mounted on a rotatable manipulator capable of translation in the x -, y -, and z -directions.

A Ge(100) sample (Si-Tech, Inc.), cut 4 – 6° off the (100) plane towards the [011] direction, 0.25–0.30 mm thick, n -type, $\rho = 5$ – $40 \, \Omega \text{ cm}$, was cut into a rectangle 13.4 mm \times 13.8 mm. A chromel-alumel thermocouple was cemented into a small hole (~ 0.5 mm dia.) drilled near one edge, using Aremco 516 high-temperature cement. The sample was mounted between Ta-foil clips attached to a Cu block and could be heated resistively to > 873 K and cooled with liquid nitrogen down to 153 K. The active area presented to the doser after mounting was 11.5 mm \times 13.4 mm. After degreasing, the Ge sample was placed in the chamber, and cleaned by several sputter-and-anneal cycles ($i_{\text{Ar}^+} = 2$ – $3 \, \mu\text{A cm}^{-2}$, $E_{\text{Ar}^+} = 500$ V, $T_{\text{anneal}} = 850$ K).

Atomic hydrogen exposures were performed by backfilling the UHV analysis chamber with H_2 to pressures of 2×10^{-8} – 5×10^{-7} Torr and heating a coiled W filament located ≈ 3 cm from the sample to 1700–1800 K. For dosing HCl or HBr, the sample was rotated to face the doser and a known amount of gas was admitted to the chamber through a calibrated aperture. Computer

calculations of flux [5] show that, for this sample geometry, 17 % of the molecules leaving the doser hit the sample, giving a flux during dosing of $(4.11 \pm 0.23) \times 10^{15} M^{-1/2} P \text{ s}^{-1}$, where M is the molecular mass (g mol^{-1}), and P is the pressure (Torr) upstream of the conductance-limiting orifice [4] during dosing. For Ge(100), one monolayer (ML) = $6.23 \times 10^{14} \text{ atoms cm}^{-2}$, and is used below to scale both doses and surface coverages.

Coverage calibrations for surface hydrogen were made using TPD of H_2S , whose adsorption as $\text{H} + \text{SH}$ [6] saturates at 0.5 monolayer (ML) [7], and which yields exclusively H_2 and GeS upon heating [8]. Coverages of HX ($\text{X} = \text{Cl}$ or Br) were made by assuming that both molecules similarly reach a saturation coverage of 0.5 ML of $\text{H} + \text{X}$.

After dosing, when the background pressure fell to about $2\text{--}3 \times 10^{-10}$ Torr, the sample was rotated to face the entrance slit of the water-cooled QMS shroud, at a distance of ≈ 0.5 cm. The temperature was ramped at a rate of 2 K s^{-1} , controlled by a Eurotherm temperature controller, and QMS signals, multiplexed for 1–3 masses, were recorded by an AT-compatible personal computer.

III. RESULTS

TPD traces for H_2 following atomic hydrogen exposures are shown in Fig. 1 for various initial coverages, Θ_0 . The nearly constant peak temperatures, T_p , together with the asymmetric peak shape at high initial coverage, indicate near first-order desorption kinetics [9]. However, the slight increase in T_p and the more symmetric peak shape at lower initial coverages demonstrate a slight departure from first-order kinetics, as also occurs for hydrogen on $\text{Si}(100)$ [10–12]. The dependence of T_p on Θ_0 is shown in Fig. 2 together with theoretical curves which are described in the next section.

Three desorption products were observed following exposure to HX ($\text{X} = \text{Cl}$ or Br): HX , H_2 , and GeX_2 , as shown in Figs. 3 and 4 for HCl and HBr , respectively. In both cases H_2 desorption occurs near 570 K after a saturation dose, as for desorption from adsorbed hydrogen alone, with T_p increasing to ≈ 580 K at initial coverages of ≈ 0.05 ML. HCl and HBr desorption occurs near 575 and 585 K at saturation initial coverage, respectively, with T_p increasing by 10–20 K at initial coverages of ≈ 0.05 ML. The weak dependence of T_p on initial coverage for both H_2 and HX desorption indicates near-first-order kinetics. The dihalide etch products GeCl_2 and GeBr_2 desorb at higher temperatures, 675 and 710 K, respectively, following saturation HX doses. In contrast to the behavior of the H_2 and HX TPD peaks, T_p for the GeX_2 peaks rose by 50–60 K at lower initial coverages, indicating approximately second-order kinetics.

Sticking probabilities for HCl and HBr were obtained from the slopes of coverage versus exposure data. The initial sticking probability, S_0 , for HCl decreased from 0.7 at 270 K to 0.05 at

400 K, while that of HBr was approximately 1.0 over the same temperature range.

Stoichiometry implies that for every H_2 molecule that desorbs, the two X atoms remaining from dissociative adsorption of HX must desorb as GeX_2 . The desorption peaks for H_2 and HX have a strong overlap while those of GeX_2 occur at higher temperature. Therefore, the branching ratio ($H_2 + GeX_2$ versus HX desorption) may be usefully described by the fraction of adsorbed hydrogen atoms which desorb as H_2 . This fraction is nearly coverage-independent at 0.6 for HCl, whereas for HBr it increases from 0.66 at saturation initial coverage to ≈ 0.9 in the low coverage limit.

IV. DISCUSSION

The present results support the new paradigm we have proposed for surface chemistry on group IV (100)-(2 \times 1) surfaces: the dimerized surface atoms [13,14] are analogous to strained digermenes (disilenes or olefins on Si(100) or diamond (100), respectively), and adsorption and desorption are analogous to molecular addition and elimination reactions, respectively [8]. The π bonds on clean surface dimers provide a driving force for *pairing* of adsorbates on the dimers [12,15]. For hydrogen the pairing enthalpy is approximately equal to the π -bond strength [12,16].

The H_2/H TPD results shown in Fig. 2 are consistent with and may be interpreted using our doubly-occupied dimer model [12], the exact solution to a lattice gas model which incorporates preferential pairing of adsorbates on dimers but neglects interactions between dimers. The coverage of hydrogen which is paired on surface dimers ("doubly-occupied" dimers) is given by [12,17]

$$\Theta_2 = \Theta - \frac{2\Theta(1-\Theta)}{[1 + 4(1/x-1)\Theta(1-\Theta)]^{1/2} + 1} \quad (1)$$

where Θ is the instantaneous total coverage of hydrogen,

$$x \equiv \exp(-\Delta H_{\text{pair}}/RT), \quad (2)$$

ΔH_{pair} is the pairing enthalpy for surface hydrogen, R is the gas constant, and T is the temperature. We assume the desorption rate of H_2 is given by

$$\text{desorption rate} = -\frac{d\Theta}{dt} = k \Theta_2 \quad (3)$$

i.e., that recombinative desorption occurs between H atoms paired on surface dimers [11,12,15,18]. Assuming that the preexponential factor for k is $2 \times 10^{15} \text{ sec}^{-1}$, as was found in a recent study of H_2 desorbing from Si(100) which took H-atom pairing into account in the analysis [19], we estimate an activation energy of 42 kcal/mol from the TPD peak temperature [9] at high initial coverage. The dependence of T_p on Θ_0 predicted by the model is shown in Fig. 2 for several assumed values of

ΔH_{pair} . By comparing the experimental and model results, we estimate ΔH_{pair} to be 4-5 kcal/mol for H on Ge(100), which is slightly less than the 6 kcal/mol obtained [12,19] for H on Si(100).

The high sticking probabilities for HCl and HBr imply a negligible activation energy for adsorption and suggest four-center transition states, as suggested previously for H₂S and H₂O on Ge(100) [8]. The decrease of S_0 for HCl with surface temperature is analogous to the behavior seen for H₂O on Ge(100) [8,20] and suggests the existence of a mobile physisorbed precursor state [21]. The larger value of S_0 for HBr than for HCl is explainable by the longer, weaker H-X bond and by transition-state arguments analogous to those comparing the adsorption of H₂O and H₂S on Ge(100) [8].

The desorption kinetics of H₂ from HX are nearly indistinguishable from those of H alone, as well as from H₂S and H₂O [8]. This independence of the desorption kinetics on the presence of coadsorbed Cl, Br, O, or S implies that desorption is a highly localized process on Ge(100), which contrasts strongly with desorption kinetics on metal surfaces.

The desorption kinetics of HX and GeX₂ are described in detail elsewhere [22]. The presence of two types of atoms (H, X), three types of pairing (H+H, H+X, X+X), and three desorption channels necessitates a generalization of the doubly-occupied dimer model. Nonetheless, it seems clear that the close similarity of the behavior of HX to that of H₂ can be accounted for by pairing of H and X atoms on surface dimers, implying that preferential pairing of adsorbates on group IV (100) surfaces is a general phenomenon and is not confined to hydrogen. The pairing enthalpy for H+X need not be equal to that of H+H (4-5 kcal/mol), however, because of the possibility of steric and electrostatic interactions and bond polarization effects. The near-second-order desorption kinetics for GeX₂ suggests that ΔH_{pair} for X+X is small.

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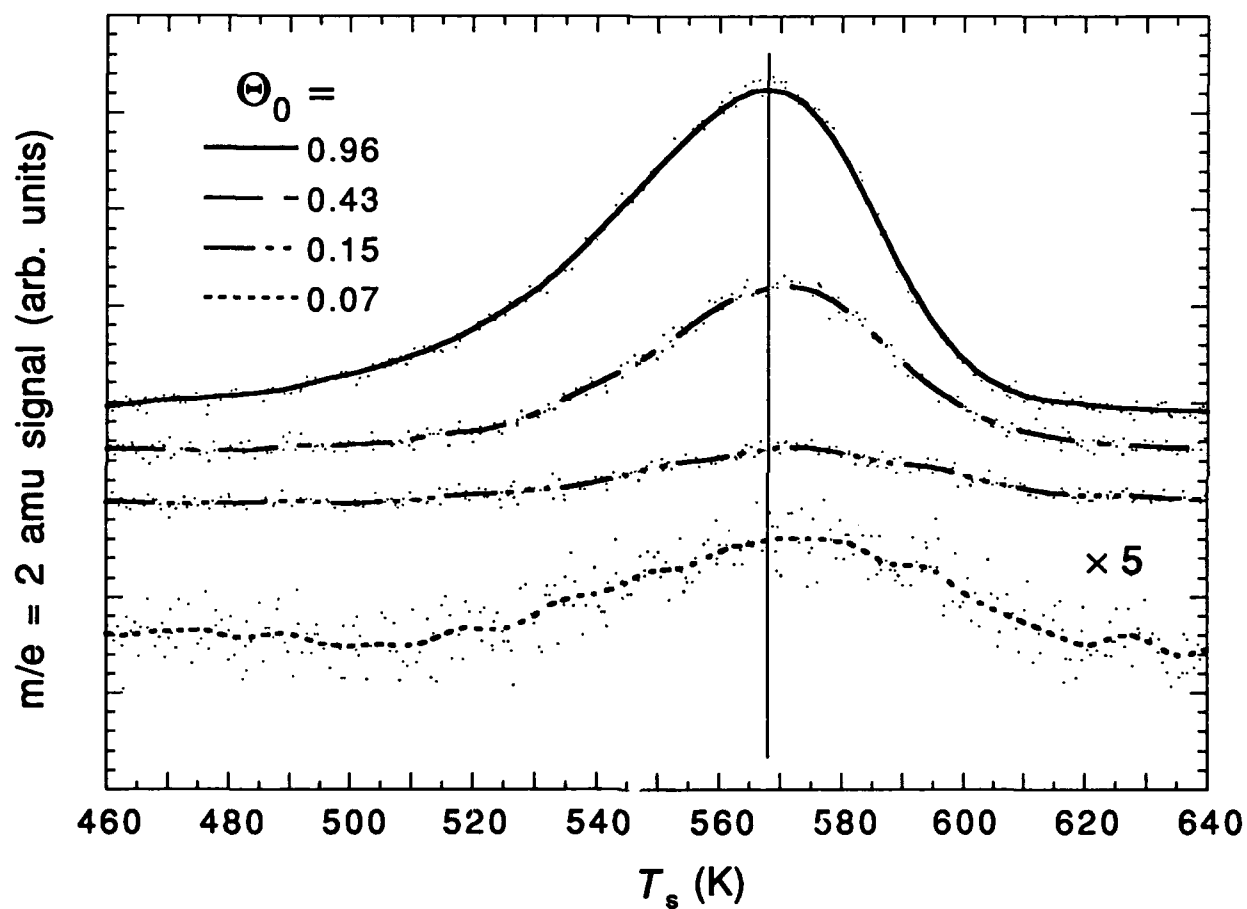


Fig. 1. Temperature-programmed desorption (TPD) data for H_2 following exposures to atomic hydrogen. The initial hydrogen coverage in monolayers, Θ_0 , is indicated for each trace.

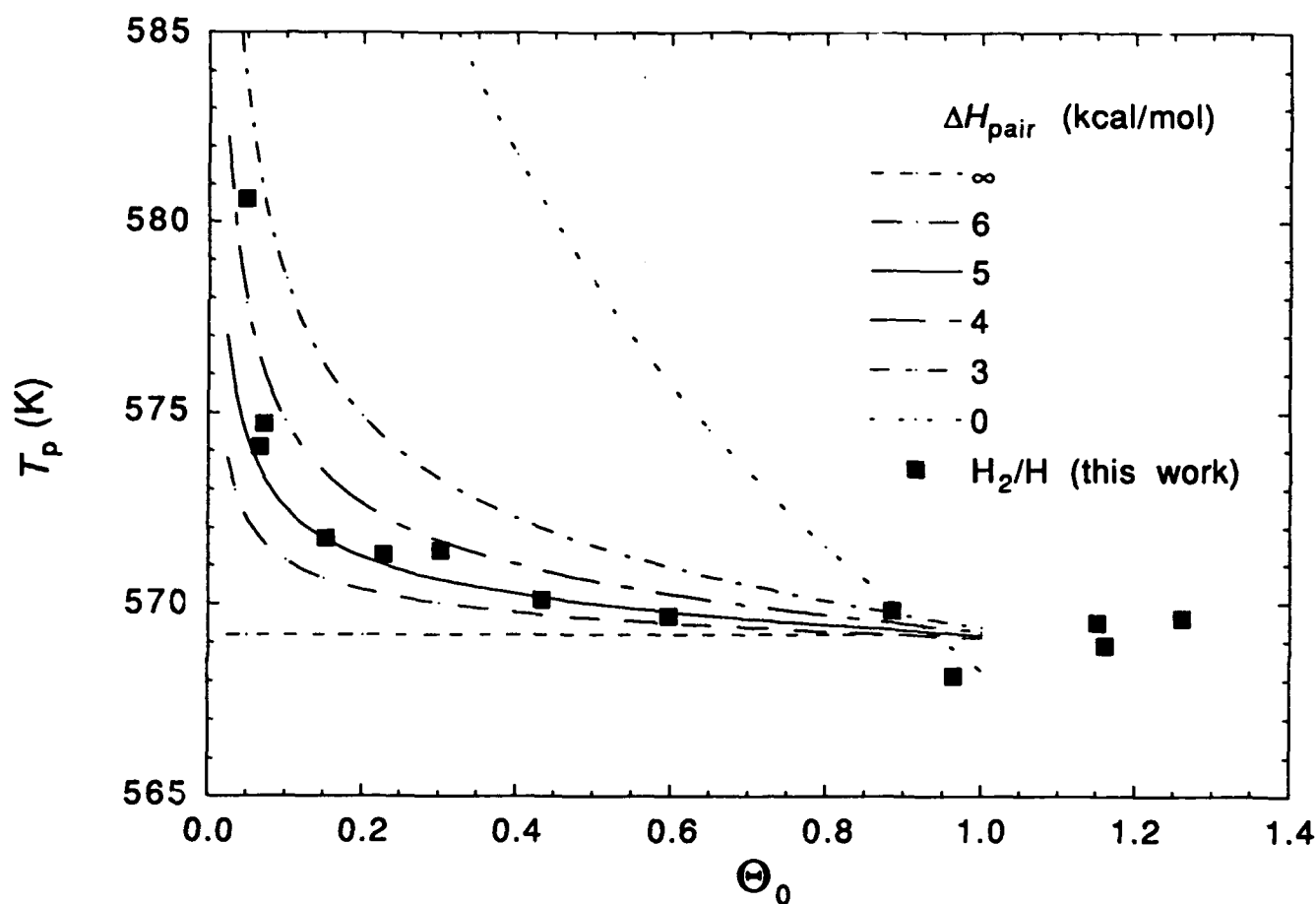


Fig. 2. Dependence of TPD peak temperature on initial coverage, as a parametric function of ΔH_{pair} . T_p was calculated using an activation energy of 42 kcal/mol and a preexponential factor of $2 \times 10^{15} \text{ s}^{-1}$ for k and a heating rate of 2 K s^{-1} .

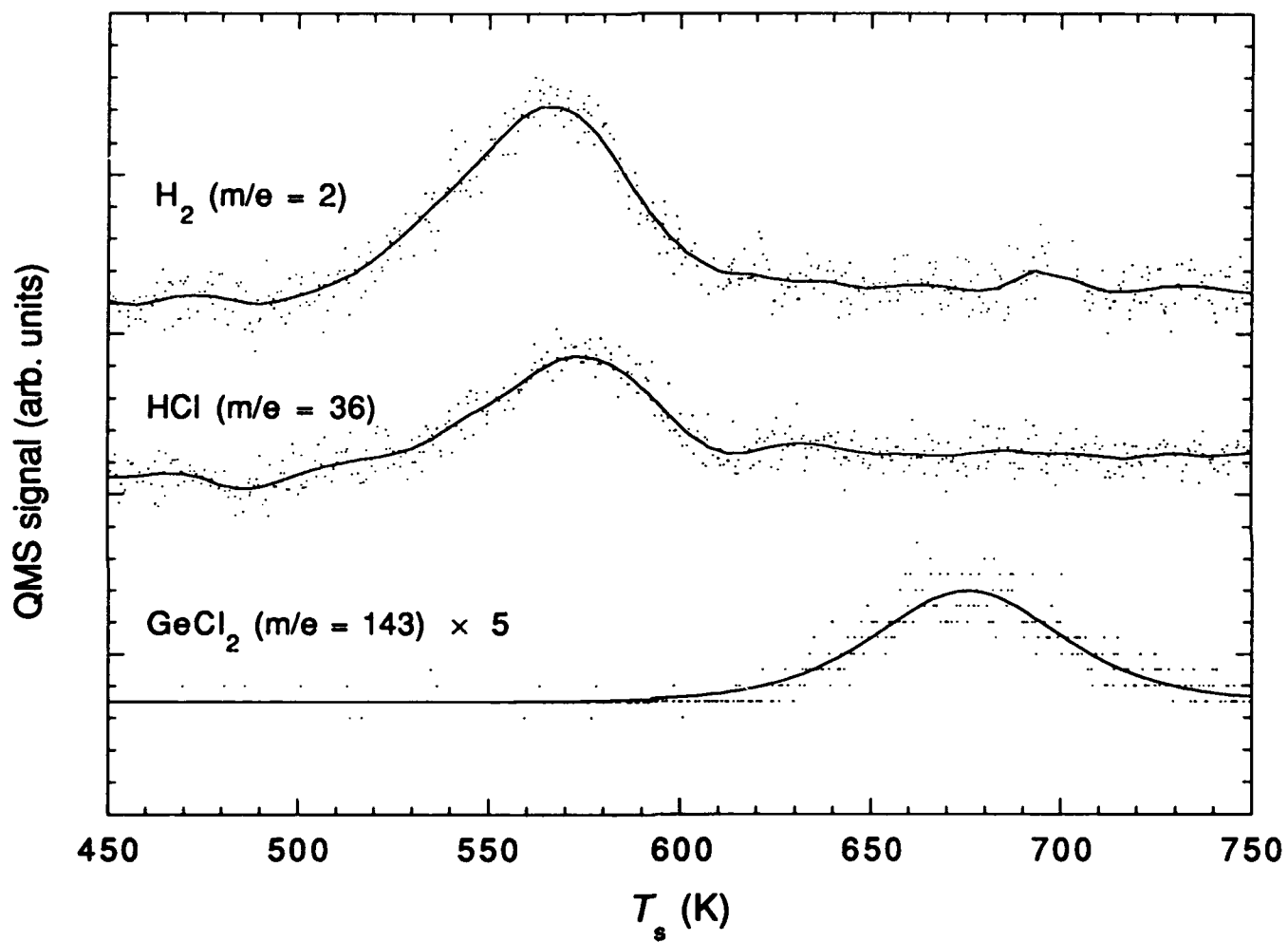


Fig. 3. Multiplexed TPD spectrum of desorption products from Ge(100) following a saturation dose of HCl.

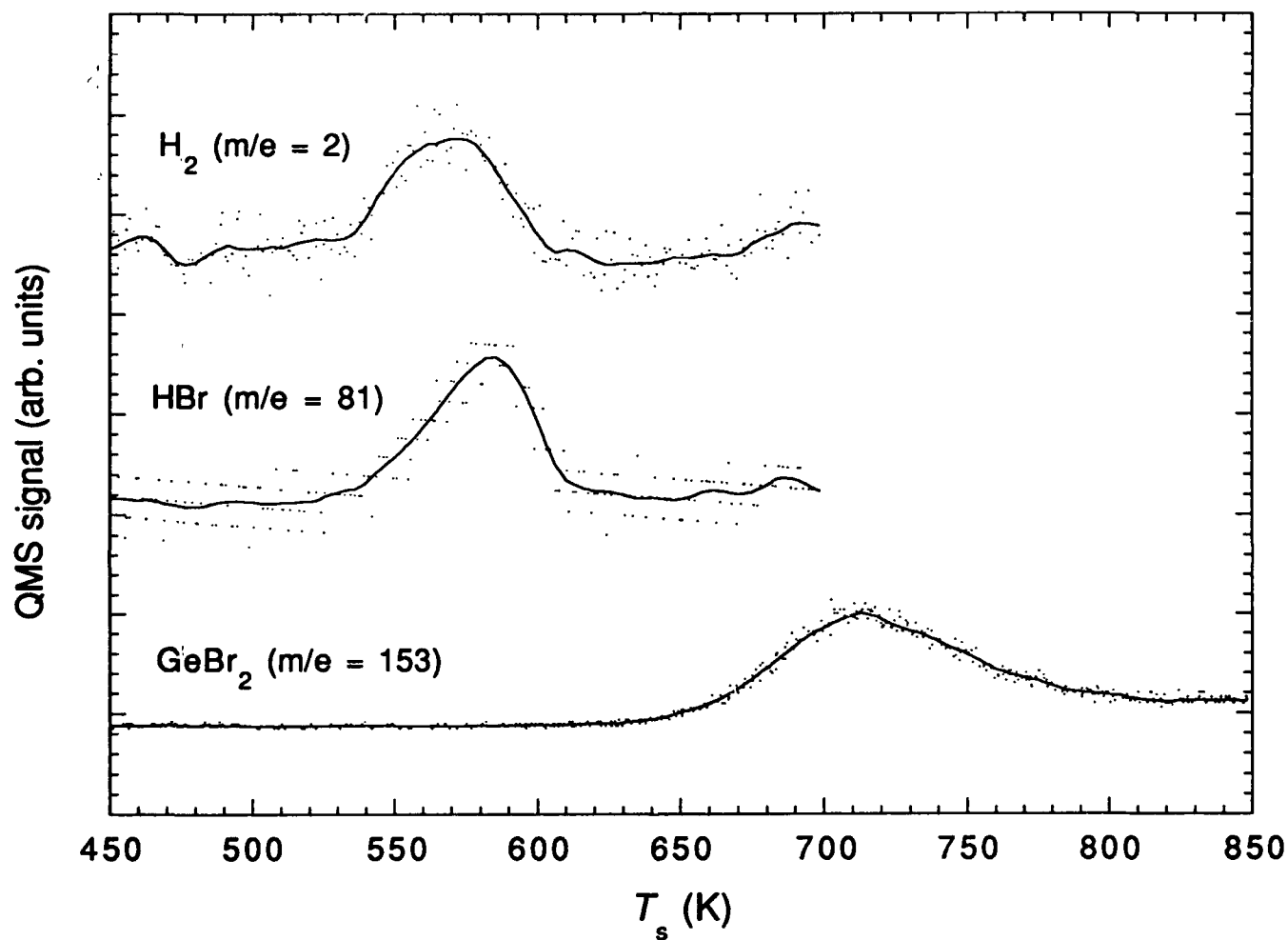


Fig. 4. Multiplexed TPD spectrum of desorption products from Ge(100) following a saturation dose of HBr. Improved signal-to-noise ratio was achieved by monitoring the $GeBr^+$ cracking fraction of $GeBr_2$.